

Irreversibility of proton conductivity of Nafion and Nafion–Titania composites at high relative humidity

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Abstract The temperature dependence of the proton conductivity of Nafion and Nafion–Titania composite in the hydrated state is investigated. The proton conductivity of Nafion–Titania measured in two successive heatings displays irreversibility, a behavior also observed in bare Nafion. The relationship between the proton transport and the dynamics of α -relaxation as proved by dielectric spectroscopy is discussed for Nafion and the composite electrolytes. The results indicate that in the first heating, the proton conductivities of Nafion and Nafion–Titania are modulated only by the glass transition of the ionomer, whereas in the second heating both the α -relaxation and the polymer glass transition are coupled to the charge transport. Such features are important for the development of high-performance electrolytes for high-temperature proton exchange membrane fuel cells.

Keywords Polymer electrolyte fuel cells · Membrane · Ion conductivity · Ionomer

Introduction

The proton conductivity of perfluorinated ionomer membranes has been investigated upon several aspects, such as, ion molar content, morphology, synthesis and preparation, temperature, and water content [1, 2]. However, relatively less effort has been devoted to study the irreversibility of the proton conductivity of Nafion usually observed when

consecutive electrical measurements are carried out at temperatures close to fuel cell operation [3, 4]. The characterization of the irreversibility on the proton conduction of Nafion-based electrolytes is fundamental for the understanding of the durability of such electrolytes in polymer electrolyte fuel cells as well as the temperature/shape memory effects in electro-mechanical actuators [4–7]. Fuel cells usually work at temperatures higher than $T > 80$ °C under successive heating–cooling cycles, which were reported to decrease the fuel cell performance pronouncedly [8].

The proton conductivity of Nafion displays distinct temperature dependences for measurements carried out in two consecutive heatings [9]. In the first heating, the proton conductivity follows an Arrhenius behavior from ~ 40 to 90 °C and a non-Arrhenius conductivity upturn at $T > 90$ °C associated with the Vogel–Tamman–Fulcher (VTF) behavior [9]. In the second heating, such conductivity upturn is absent and the temperature dependence is nearly linear in the entire temperature range ($T \sim 40$ – 180 °C) [9]. The difference of the proton conduction behavior in both heatings can be attributed either to the irreversibility on the ionomer water uptake or to the irreversible morphology changes of Nafion [6, 7, 10]. The former is associated to the degree of dissociation of the protonic charges on increasing water sorption, whereas the latter is associated with the relaxation of the ionomer structure at temperatures above α -transition. At high temperatures ($T > 100$ °C), the water uptake of Nafion is higher and the water uptake at room temperature is not recovered when the sample is cooled down [4, 7, 11]. In addition, it has been reported that Nafion undergoes an irreversible morphology transition at temperatures above the α -transition ($T \sim 110$ – 120 °C) [10]. Both the irreversibility of the water uptake and the ionomer morphology

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are likely to affect the proton conductivity behavior at high temperatures.

Previous studies of the impedance and conductivity spectrum of Nafion at low and high relative humidity allowed separating contributions arising from the absorbed water from the chain motion in the polymer matrix [10, 12]. The impedance spectroscopy (IS) study of nearly dry Nafion membranes, in which the protonic charges are mostly coordinated to the polymer chains, was useful in revealing that there is a correlation between the proton conductivity and the α -relaxation [10, 12]. These measurements provided new insights into the mechanisms involved in the proton conductivity of hydrated samples. The IS study of hydrated samples evidenced that the proton conductivity possess two distinct regimes: one at frequencies close to the α -relaxation frequency (low frequency $<10^{-1}$ Hz) and the other at frequencies close to the high-frequency dc conductivity of Nafion ($\sim 10^6$ Hz). The high-frequency conductivity followed the VTF empirical law and was attributed to the cooperative motion of the protonic charges and the main chains of Nafion at $T > T_g$. The low-frequency dc proton transport was observed to be influenced by the α -transition ($T \sim 120$ °C), and exhibited a similar temperature dependence of the α -relaxation [10]. However, at $T > 110$ °C, the increase of the water content with increasing T follows a more linear behavior up to 180 °C [10]. The mismatch between the temperature dependence of the water uptake and proton conductivity at high-temperature evidences that at high temperatures the proton conductivity is mostly associated with the dynamics of Nafion relaxations rather than the water uptake [10].

Recent measurements of proton conductivity on Nafion-based composites performed at high T have shed some light on the relation between water uptake and proton conductivity [13]. The water uptake (v) of Nafion–Titania composites (NT) prepared by sol–gel ($v \sim 20$ vol %) is significantly lower than that of Nafion ($v \sim 40$ vol %) [13]. In addition, it is interesting to consider that NT composites exhibit a significant increase of the water uptake for $T > 130$ °C, such a temperature is considerably higher than that observed for Nafion ($T > 100$ °C) [10, 13]. Nevertheless, the deviation from the Arrhenius behavior of the proton conductivity of NT composites occurs at the same temperature as that observed for Nafion ($T \sim 90$ °C) [9, 13]. Such a feature suggests that the mechanism of proton conduction is not only dependent on the water content at high temperatures.

In this context, the present study investigates the irreversibility of the temperature dependence of the proton conductivity, when measured in consecutive heatings. The relationship between water content and the relaxation dynamics on proton transport of perfluorosulfonate ionomers was studied by measuring the proton conductivity in a

wide range of temperature and frequency. The study of the proton conductivity of Nafion–Titania at different frequencies revealed that the irreversibility of high-frequency proton conductivity is an outcome of the coupling between the ion transport with the α -relaxation.

Experimental

Commercial Nafion 115 membranes ($EW = 1100$ g eq $^{-1}$) were obtained from DuPont. The membranes were pretreated by standard cleaning and activation protocols [13]. Hydrated samples (in the protonic form) were characterized without previous thermal treatment to avoid morphological changes.

Titania (anatase) nanoparticles (of ~ 4 – 6 nm in diameter [8, 13]) were synthesized in situ into Nafion 115 by the sol–gel method with a nominal concentration of $C = 20$ vol% [13]. The synthesis of Nafion–Titania composites (NT) consists basically in swelling the N115 in ethanol for 1 h at room temperature to facilitate the access of titanium tetraisopropoxide (TIP/1 mol L $^{-1}$, Aldrich). Next, a peptizing agent is added to the solution to promote the controlled hydrolysis and condensation of nanoparticles. The formation of titania is promoted by the addition of hydrogen peroxide (30 vol%) to the solution in a 6.5:1 (H $_2$ O $_2$:TIP) ratio. The condensation (crystallization) is carried out in an oven at 70 °C for 24 h. After the synthesis, the composite samples are washed firstly in H $_2$ SO $_4$ (0.5 mol L $^{-1}$) for 1 h, and finally in deionized water.

Impedance (dielectric) spectroscopy (IS) measurements were performed on samples using a specially designed airtight sample holder [3, 9]. Temperature controllers connected to band heaters placed externally around the cylindrical chambers are monitored by thermocouples (type K) inserted inside its metallic walls. The constructed sample holder allows controlling both the temperature (from room temperature up to $T \sim 200$ °C) and relative humidity. Nafion samples were sandwiched with carbon cloths, to facilitate water equilibration, between stainless steel spring-load contact terminals, insulated from the chamber walls. Before studying the electric properties of the ionomer, several experiments were performed to ensure the correct assessment of the bulk properties of the sample under investigation. Some of the parameters checked were different electrode materials (platinum, gold, carbon cloth), different membrane thicknesses, and the short-circuited sample holder. Such series of experiments are important to separate contributions arising from the sample holder (and connection cables) and electrodes from the sample itself. In a recent report, small angle X-ray scattering (SAXS) measurements were performed as a function of time under an applied dc potential in order to verify whether electrode

polarization is observed in IS data of Nafion. Such experiments revealed morphology changes under the applied potential in the same timeframe of the impedance spectroscopy measurements, further indicating that electrical data correspond to the bulk properties of Nafion samples [12].

In the experimental apparatus used for IS measurements, the *RH* of the sample chamber can be calculated by

$$RH = \rho(T_r)/P(T_c) \times 100, \quad (1)$$

where ρ is the saturated vapor partial pressure, P is the vapor partial pressure, and T_r and T_c are, respectively, the water reservoir and sample chamber temperatures. For the IS measurements as a function of *RH* and *T*, preconditioning of the sample is carried out in order to ensure equilibrium conditions. In temperature-dependent measurements, the sample was allowed to equilibrate with the water vapor for 24 h at 40 °C (*RH* = 100 %) prior to IS measurements. For the IS measurements performed as a function of *T* at constant *RH*, impedance spectra of hydrated samples were collected after at least 30 min of stabilization at each measuring temperature. In the case of measurements as a function of *RH*, the sample was stabilized for 3 h to reach the equilibrium with the sample holder environment. During the IS measurements, the equilibrium condition was assumed to be attained when the electrical resistance of the sample at a given *RH* and *T* was constant as a function of time. For measurements as a function of *RH* at *T* = 80 and 130 °C, the dry sample was positioned in the sample holder; the sample holder and the water reservoir were heated to obtain the desired *RH* according to Eq. 1. Then, the system was allowed to equilibrate for ~3 h until a constant sample electrical resistance was obtained. The IS measurement as a function of *RH* was carried out after 30 min of stabilization at each measuring *RH* with step of 5 or 10 %.

A Solartron 1260 frequency response analyzer was used in the frequency (*f*) range of 0.1–3 MHz applying an ac amplitude of 100 mV. The complex conductivity ($\sigma^* = 2\pi f \epsilon_0 \epsilon^*$) and dielectric permittivity ($\epsilon^* = \epsilon' + i\epsilon''$) representations were used throughout this study.

Results and discussion

In order to study the effects of α -transition on the irreversibility of proton conductivity, Nafion–Titania (NT) composites were evaluated in successive heatings. Figure 1 shows the temperature dependence of the high-frequency dc proton conductivity ($f \sim 10^6$ Hz) of Nafion and NT measured in two consecutive runs in the through-plane and in-plane setups. The proton conductivity of Nafion in the first heating is shown for comparison.

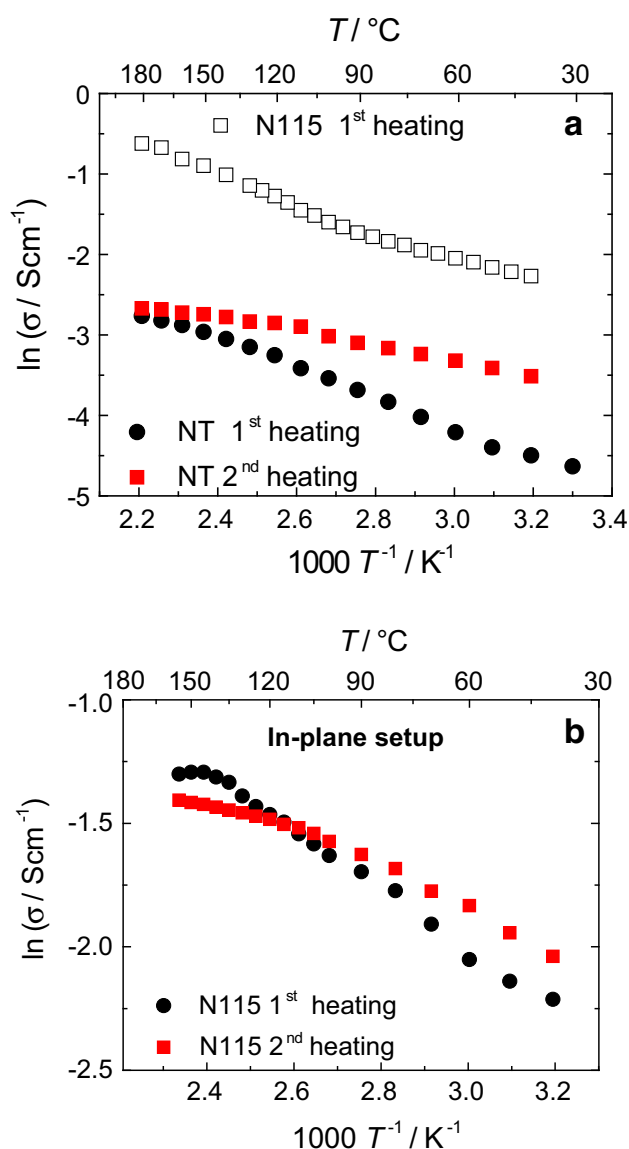


Fig. 1 Arrhenius plots for the dc conductivities (through-plane) of NT composites in two successive heatings at *RH* = 100 % (a). Arrhenius plots for the dc conductivities (in-plane) of Nafion in two successive heatings at *RH* = 100 % (b)

The proton conductivity of both the Nafion and NT composites displays similar temperature dependence. However, the conductivity of NT is lower than that of Nafion in the entire temperature range. This feature may be a result of both the lower water content of the NT composites (~20 vol%) compared to Nafion (~40 vol%) and the lower relative conductivity of the inorganic phase [13]. In the first heating, the conductivity of NT composites displays a VTF-like behavior above $T \sim 60$ °C, whereas in the second heating, a more linear temperature dependence is observed in the entire temperature range. Similar behavior was previously observed in Nafion membranes and Nafion-based composites [14, 15], in which the VTF

behavior is observed in the first heating and a nearly linear response in the second heating [9]. This feature can also be observed for the conductivity of Nafion measured in the in-plane setup (Fig. 1b). However, a marked difference is observed in the NT samples. In composites, the proton conductivity upturn occurs at lower temperature ($T > 60$ °C) than Nafion ($T > 90$ °C). Moreover, the water uptake upturn with increasing temperature occurs at $T \sim 100$ °C for Nafion and $T \sim 130$ °C for the NT composite, as reported elsewhere [13]. Therefore, the different temperatures of the upturn in the water uptake and in the proton conductivity add further evidence that the water content plays a minor role in the temperature dependence of the conductivity at high T .

It is worth noting that in the second heating, the conductivity of NT is higher than the first one in the entire temperature range. However, a different behavior was observed for Nafion membranes: the proton conductivity in the second heating is higher than the first one at low temperatures, and due to the absence of the upturn of proton conductivity at $T > 90$ °C, the proton conductivity is lower at high temperatures. The reduction of the proton conductivity at high T in the second heating was previously observed for N105 in the through-plane setup [9]. Such feature can be confirmed in the in-plane conductivity of N115 (Fig. 1b) in which the magnitude of the proton conductivity is more reliable due to the low electrolyte-electrode interface resistance compared to the electrolyte resistance [9]. In the composite sample, the conductivity is reduced with respect to the one observed for N115 due to the high concentration of the insulating phase (titania) [13]. The higher conductivity of the Nafion-Titania in the second heating may be due to a dilution effect, i.e., a reduction of the concentration of the nanoparticles in the membrane as in the second heating the sample swelled irreversibly with respect to the first heating.

In order to evaluate the influence of the α -relaxation on the irreversibility on the transport properties of Nafion-based composites, the effect of two consecutive heatings on the ac conductivity and the dielectric spectrum of NT, measured at $T = 120$ °C and $RH = 100$ %, is shown in Fig. 2.

The conductivity plots of NT composite (Fig. 2a) display the decrease of the proton conductivity with decreasing frequency in the intermediate range (10^0 - 10^4 Hz) at $T = 120$ °C, usually attributed to the universal power law response due to ion-hopping in amorphous or disordered ionic conductors [16]. In the first heating, the low- f conductivity plateau cannot be observed due to the presence of α -relaxation in a similar frequency range ($f \sim 10^{-3}$ – 10^0 Hz). On the other hand, in the second heating, as the α -relaxation shifts to higher frequency, the

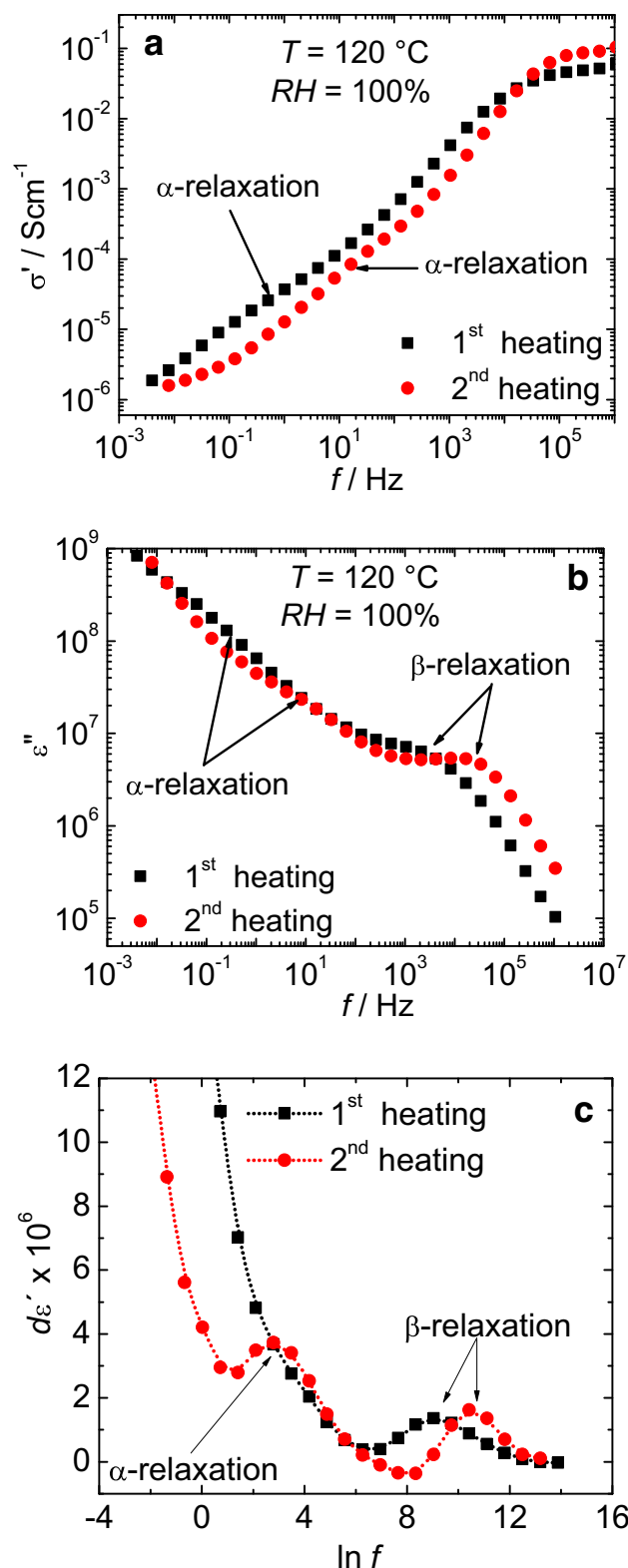


Fig. 2 Frequency dependence of ac conductivity (a); dielectric permittivity loss (b); and derivative of the dielectric constant with respect to $\ln f$ (c) for Nafion-Titania composite at $T = 120$ °C and $RH = 100$ %

low-frequency plateau becomes more apparent ($f < 10^{-1}$ Hz). In both runs, the high-conductivity plateau can be observed for $f > 10^4$ Hz. The decaying function of the σ' with decreasing f was attributed to a distribution of potential wells, which represent energy barriers for the ion transport along a percolating path within the polymer microstructure [16]. The conductivity plateaus attributed to α and β -relaxation can be attributed to two characteristic potential wells, which can be assigned to the charge transport along the average length and distance between Nafion polymeric aggregates, respectively [10, 17].

Figure 2b shows the dielectric permittivity loss as a function of frequency for NT composites in the first and second heatings. In the dielectric loss curve, it can be identified the α ($f < 10^1$ Hz) and β ($f \sim 10^4$ Hz) relaxations, evidencing the displacement to high frequencies of both relaxations in the second heating. The displacement of the α -relaxation is not easily observable due to the dc conductivity increase at low frequencies ($f < 10^{-1}$ Hz). In order to reveal the high- f displacement of α -relaxation, the dielectric loss was obtained from the Kramers–Kronig transform $\varepsilon''(f) \approx d\varepsilon'/d\ln f$, as shown in Fig. 2c. The Kramers–Kronig relation extracts the $\varepsilon''(f)$ from the $\varepsilon'(f)$, which is free from dc conductivity contributions [18]. In Fig. 2c, the displacement of α -relaxation to higher frequencies is confirmed. The displacement of the α and β -relaxations to higher frequencies in the second heating can be either associated with an increase of the low- f conductivity or to a reduction of the average length (α -relaxation) and the distance (β -relaxation) among Nafion polymeric aggregates. As the low- f conductivity ($f < 10^{-2}$ Hz) in the first and second heatings is similar (Fig. 2a), the high- f displacement of α and β -relaxations can be assigned to a reduced length and distance of the polymeric aggregates, respectively, during sample heating.

The high- f displacement of α -relaxation suggests that the irreversibility shown in proton conductivity data (Fig. 1) is mainly due to the correlation of the proton conductivity with the α -transition of the ionomer matrix in the second heating. In the first heating, the proton conductivity of hydrated Nafion displays the VTF behavior at $T > 90$ °C due to the cooperative motion of charges with the main chains above the glass transition [10]. Fig. 2a shows that, in the second heating, the α -relaxation is affecting the proton conductivity at higher frequencies indicating that the migration of protons is modulated by both α and glass transition.

As the proton conductivity of ion-containing polymers is dependent on the cooperative motion of the polymer main chains and of the ion transport, the change of the temperature dependence of proton conductivity observed in the first and second heatings can be better understood by considering the influence of the dynamics of Nafion α -

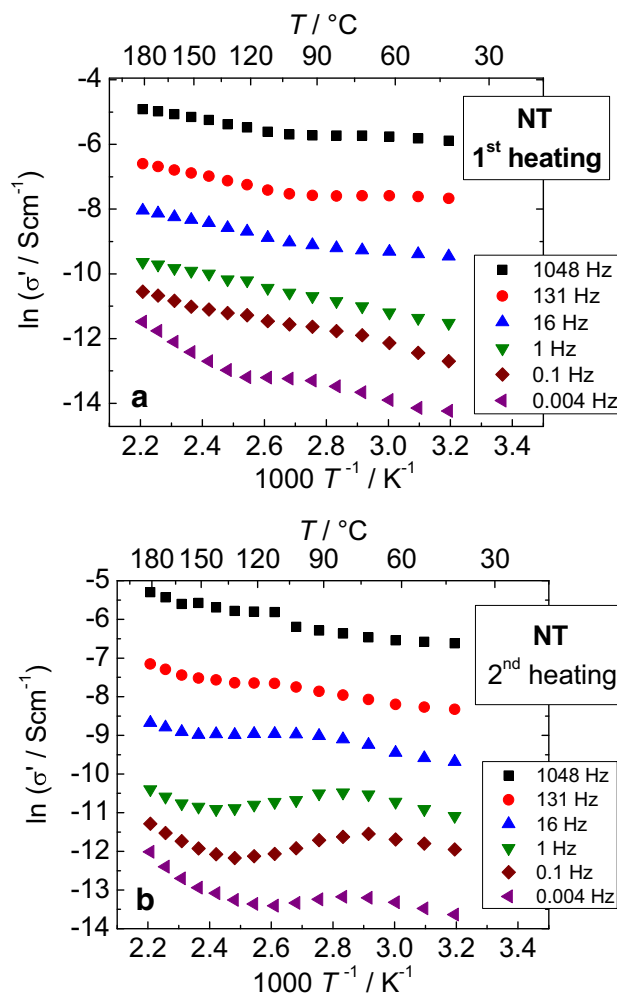


Fig. 3 Arrhenius plots for the ac conductivities (through-plane) of NT composites for the first (a) and second (b) heatings

relaxation at lower frequencies. Figures 3a, b show the temperature dependence of proton conductivity of NT composites within the frequency range of α -relaxation.

In the first heating, the proton conductivity for $f > 1$ Hz displays both the Arrhenius and VTF regimes. For $f < 1$ Hz, the proton conductivity is coupled to the α -relaxation. In the first heating, the α -relaxation of NT occurs at very low frequencies ($f < 1$ Hz) and the proton conductivity exhibits no noticeable changes at frequencies higher than 1 Hz. In this context, it is proposed that the high- f proton conductivity is coupled to the polymer glass transition (T_g) giving rise to the VTF behavior at high T [18, 19]. Such behavior is commonly observed in ion-containing polymers in which the proton conductivity is only governed by the glass transition dynamics [18]. However, in the second heating (Fig. 3b), the VTF temperature dependence cannot be identified and the influence of α -relaxation on the proton conductivity can be observed at a much higher frequencies ($f < 1048$ Hz).

The characterization of the electrical properties of NT composite aided the separation of the contributions due to motion of polymer chains, since NT sample absorbs a lower amount of water and has different relaxation frequencies for α and β -relaxations compared to Nafion. It is worth noting that the change from the non-linear temperature dependence observed in the first heating to a more linear one in the second heating is linked to the displacement of α -relaxation to high frequencies. This feature indicates that the linear temperature dependence of the proton conductivity observed in the second heating in Fig. 1 can be a result of the modulation of the charge transport in Nafion due to both α relaxation and the glass transition.

Nonetheless, some recent reports have evidenced that the changes in water sorption can be intimately associated with Nafion relaxations [20, 21]. It has been generally accepted that the water uptake capacity of ionomer samples is dependent on the flexibility of polymer chains, which allows polymer expansion upon water sorption. Such an effect increases both the proton dissociation and conductivity of the ionomer [11, 20, 21]. In this context, the separation of the main factor influencing the proton conductivity of Nafion becomes a hard task. However, dielectric spectroscopy measurements provide a better understanding on this intricate relation between the relaxations, water content, and conductivity. Figure 4a shows the dielectric loss as a function of relative humidity for Nafion–Titania composite, Fig. 4b shows the corresponding high- f dc proton conductivity as a function of relative humidity for Nafion and Nafion–Titania, and Fig. 4c shows an expanded view of the high RH-range of the conductivity plot shown in Fig. 4b.

In Fig. 4a, only the β -relaxation ($f \sim 10^3$ Hz at RH ~ 10 %) is present in the dielectric spectra at low RH (RH < 50 %). The RH-dependence of β -relaxation of Nafion–Titania is similar to the one reported for Nafion [22], exhibiting a high- f displacement with increasing RH up to ~ 60 %, and reversing its trend for RH > 60 %. The displacement of the β -relaxation to lower frequencies for RH > 60 % is attributed to the increase in the correlation distance among Nafion polymeric aggregates due to the increase in water uptake [10]. It is interesting to note that at RH > 60 %, the α -relaxation appears in the dielectric spectra at low frequencies and shifts to higher frequencies with increasing RH. The results shown in Fig. 4b suggest that the coupling between α -relaxation and the proton conductivity of Nafion and NT composite at high temperature and high relative humidity is in consonance with the σ – α relationship shown in Figs. 2 and 3 of the manuscript.

The coupling between the proton conductivity and the Nafion relaxations can be understood considering the degree of dissociation of the protonic charges in fully

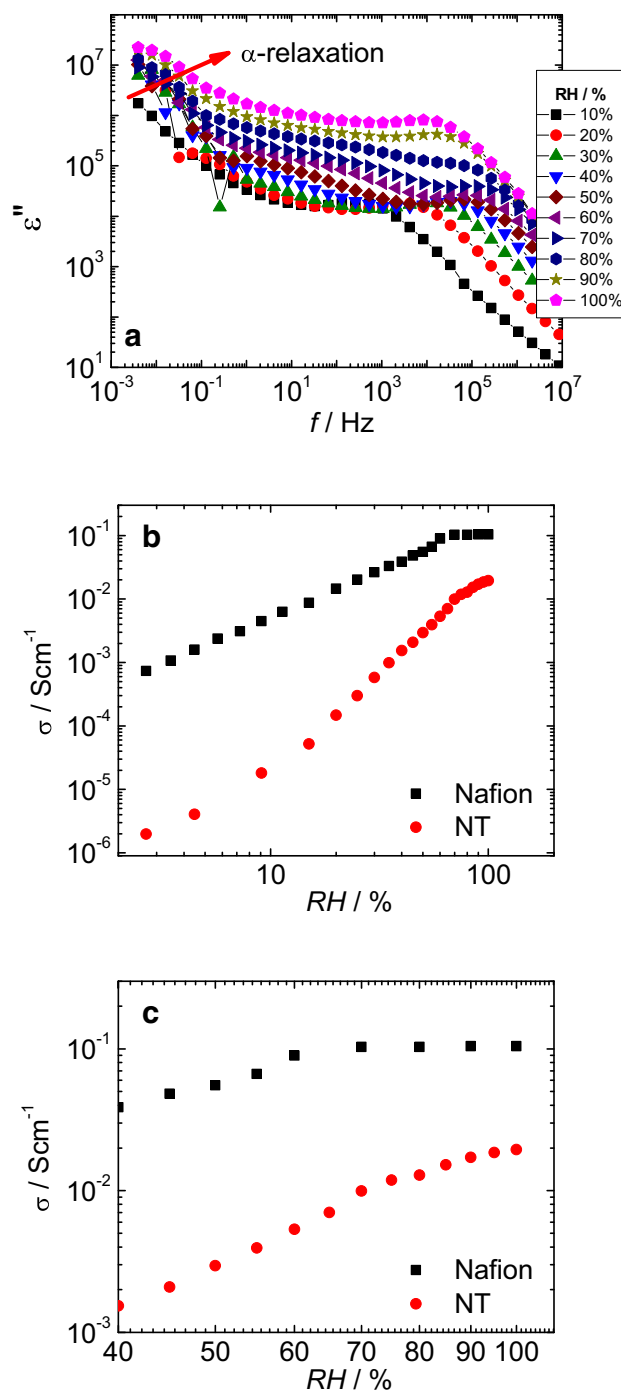


Fig. 4 Dielectric loss (a), high- f dc proton conductivity (b) and an expanded view of (c) for Nafion–Titania (through-plane) as a function of relative humidity at 130 °C

hydrated Nafion. Previous reports offered some insight into this phenomenon [23]. The authors have shown that during the conductivity measurements at high relative humidity, a maximum of four water molecules are solvating the protonic charges, indicating that the protons are not fully dissociated from sulfonic groups. As such, it is reasonable

to assume that if charges are not fully dissociated from sulfonic groups, the proton conduction must exhibit a dependence on both water content and chain motion.

Previous dynamic mechanical analysis (DMA) studies showed that for temperatures lower than the α -transition, the mobility of Nafion chains is restricted by ionic crosslinks between condensed SO_3H in the dry state [24]. The dynamics of α -relaxation and the glass transition dictate the polymer elastic forces that counterbalance the membrane swelling. However, it is interesting that it can be identified in the literature at least three divergent interpretations of the relationship between the polymer viscoelastic and the swelling properties of Nafion [11, 17, 25–28]. One of the models, propose that the condensed SO_3H existing in Nafion in the dry state provides the driving force for the membrane swelling, and the SO_3H crosslinks are dismantled as the water content increases [27]. It is reasonable to consider that in this model the α -transition only exists in the dry state as it corresponds to the destabilization of the SO_3H dipoles. With the absence of such relaxation, the polymer chains have higher flexibility and, therefore, it would result in a membrane with a high ability to absorb water [27]. However, it has been reported by different authors using mechanical and electrical analyzes such as DMA [11, 29] and dielectric spectroscopy [10, 12, 17] that α -transition exists even in the hydrated state of Nafion. Moreover, such transition “stiffens” the hydrated polymer thereby increasing the internal pressure of the membrane [11, 28]. This result is in good accordance with Fig. 4a, which evidenced the presence of α -relaxation in the humid state of Nafion. The presence of α -transition has been interpreted as a decrease of the protonic charge dissociation or increased degree of associated ionic crosslinking [11]. On the other hand, another possible approach is the presence of condensed counterions in hydrated Nafion membranes [17, 25, 26]. More recently, it was shown that these electrostatic physical crosslinks are possible to exist even in hydrated Nafion membranes due to the presence of condensed counterions [10, 12, 17]. In the hydrated state, there is a fraction of dissociated free counterions, which contributes to high swelling and conductivity of Nafion, and a fraction of condensed counterions, which does not contribute considerably to the water swelling and increase the mechanical resistance of Nafion [10]. These condensed counterions exist in the hydrated form in order to minimize the electrostatic repulsions among sulfonic acid groups of Nafion [25, 26]. At temperatures above α -transition, these electrostatic crosslinks are destabilized allowing a higher water sorption capacity of Nafion. This finding is in good agreement with the pronounced water content of Nafion at $T > 110^\circ\text{C}$, due to the release of the electrostatic crosslinks at temperatures above α -transition

($T \sim 120^\circ\text{C}$) [10, 11]. It is worth noting that the two models for hydrated Nafion—the full dissociation of ionic groups and counterion condensation of ionic groups—indicate that there is electrostatic crosslinking at high T and high RH. However, the existence of α -relaxation in the hydrated Nafion shown in Fig. 4a supports the swelling model that takes into account the counterion condensation. It is the disruption (and not the formation) of the electrostatic crosslinks that allows a higher water sorption for $T > 110^\circ\text{C}$ in Nafion.

Additionally, there is another difference between Nafion and Nafion–Titania composites that allowed discerning sigma–alpha relationships. The α -relaxation of the NT composite displaces to higher frequencies in the entire humidity range at $T = 130^\circ\text{C}$ (Fig. 4a). However, the α -relaxation of Nafion displaces to higher frequencies up to RH $\sim 60\%$, above which the relaxation displaces to lower frequencies. In accordance with the analysis proposed in this study, at $T = 130^\circ\text{C}$, the motion of Nafion chains is not restricted by the α -relaxation, while the motion of the NT composite chains is. This result is in good agreement with the upturn of water uptake capacity at $T > 110^\circ\text{C}$ for Nafion and at $T > 130^\circ\text{C}$ for the NT.

The results shown in Figs. 4a, b indicate that α -relaxation is present even in the hydrated sample and is possibly restricting the motion of the polymer chains and possibly restricting the water swelling [11], thereby reducing the proton conductivity dependence on the relative humidity. This feature can be visualized in the expanded views of the high RH-range of the conductivity plot (Fig. 4c). Another possible effect causing the reduction of the proton conductivity dependence on RH is the condensation of protons in sulfonic acid groups due to strong electrostatic repulsions among sulfonic acid groups at high RH. Therefore, the effect of water is beneficial up to a certain content; above a critical water content the displacement of α -relaxation to higher frequencies takes place, thereby reducing the high-frequency dc conductivity of Nafion (Fig. 1b).

These results indicate that the proton conductivity is strongly dependent on the water content at RH $< 60\%$. However, at high water content and high temperatures, the proton conductivity becomes more predominantly dependent on the Nafion relaxations. These results can be a link to understand the reduction of the proton conductivity of Nafion at high relative humidity, which is observed above a crossover temperature of $T \sim 120^\circ\text{C}$ [3, 4, 6, 30]. This reduction of Nafion proton conductivity coincides with the α -transition temperature at RH $\sim 100\%$ ($T \sim 120^\circ\text{C}$) [10]. According to previous report on the proton transport of Nafion, it was shown that the proton diffusion coefficient decreases for $T > 120^\circ\text{C}$ as a result of a reduced mobility of Nafion chains at temperatures above α -transition [10].

Conclusions

The study of the transport properties of Nafion and Nafion–Titania by dielectric spectroscopy evidenced that irreversibility of the proton conductivity at high temperatures is mainly related to the displacement of the α -relaxation to higher frequencies in the second heating. As the α -relaxation is shifted to frequencies higher than the frequency of the dc conductivity plateau observed at low frequencies ($f < 10^{-2}$ Hz), the proton conductivity is coupled to both the ionomer glass transition and the α -relaxation. Such features are important to advance the understanding of Nafion-based composites aiming for application in high-temperature polymer electrolyte fuel cells.

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